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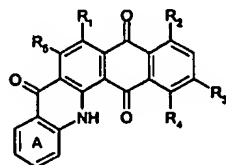
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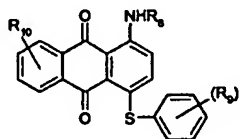
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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PIGMENT/DYE MIXTURES



(I)



(II)

(57) Abstract: A composition comprising (A) at least one nickel complex pigment and (B) at least one disperse dye of formula (1) or (2) wherein R₁ is hydrogen, hydroxy or a radical -NHCO-R₆ wherein R₆ is C₁-C₆alkyl or unsubstituted or C₁-C₄alkyl- or halo-substituted phenyl, R₂ is hydrogen, hydroxy or a radical W-R₇, wherein W is -NHCO- or -S- and R₇ is C₁-C₆alkyl or unsubstituted or C₁-C₄alkyl- or halo-substituted phenyl, R₃ is hydrogen, R₄ is hydrogen or hydroxy, R₅ is hydrogen, or R₃ and R₄ together form the radical of formula wherein the rings A and B, independently of one another, may carry further substituents, R₈ is hydrogen or -CO-C₂-C₆alkyl wherein the C₂-C₆alkyl radical may be substituted by carboxy, or a radical wherein R₁₁ is hydrogen, C₁-C₄alkyl, hydroxy, carboxy or halogen, R₁₂ is hydrogen, C₁-C₄alkyl or halogen and R₁₃ is hydrogen or C₂-C₃alkyl or, when R₁₀ is halogen, R₁₃ may be methyl, R₉ is hydrogen or halogen, R₁₀ is hydrogen or halogen, and n is a number 0, 1 or 2, with the proviso that R₉, R₁₀, R₁₁, R₁₂ and R₁₃ are not all simultaneously hydrogen, is suitable for the dyeing or printing of semi-synthetic or synthetic hydrophobic fibre materials and in the production of coloured plastics or polymeric colour particles.

Pigment/dye mixtures

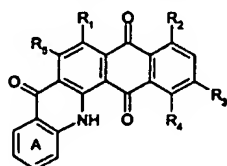
The present invention relates to a composition comprising a nickel complex pigment and a disperse dye and to the use of such a composition in the dyeing or printing of hydrophobic fibre materials and in the production of coloured plastics or polymeric colour particles.

The use of nickel complex pigments as disperse dyes in the dyeing of polyester fibres is known, for example, from WO 02/057537 and WO 02/055786. The dyeings thereby obtained are distinguished by good general fastness properties, especially a high level of fastness to light and to wetting.

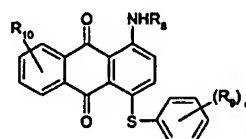
Surprisingly it has now been found that a considerable further improvement in those good properties can be obtained by the addition of specific disperse dyes.

The present invention relates to a composition comprising

- (A) at least one nickel complex pigment and
 (B) at least one disperse dye of formula (1) or (2)



(1),



(2),

wherein R₁ is hydrogen, hydroxy or a radical -NHCO-R₆ wherein R₆ is C₁-C₆alkyl or unsubstituted or C₁-C₆alkyl- or halo-substituted phenyl,

R₂ is hydrogen, hydroxy or a radical W-R₇ wherein W is -NHCO- or -S- and R₇ is C₁-C₆alkyl or unsubstituted or C₁-C₆alkyl- or halo-substituted phenyl,

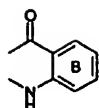
R₃ is hydrogen,

R₄ is hydrogen or hydroxy,

R₅ is hydrogen, or

R₃ and R₄ together form the radical of formula

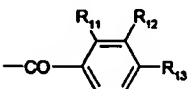
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, wherein the rings A and B, independently of one another, may carry

further substituents,

R_8 is hydrogen or $-\text{CO}-\text{C}_2-\text{C}_6\text{alkyl}$ wherein the $\text{C}_2-\text{C}_6\text{alkyl}$ radical may be substituted

by carboxy, or a radical  wherein R_{11} is hydrogen, $\text{C}_1-\text{C}_4\text{alkyl}$,

hydroxy, carboxy or halogen, R_{12} is hydrogen, $\text{C}_1-\text{C}_4\text{alkyl}$ or halogen and R_{13} is hydrogen or $\text{C}_2-\text{C}_3\text{alkyl}$ or, when R_{10} is halogen, R_{13} may be methyl,

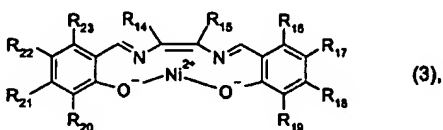
R_9 is hydrogen or halogen,

R_{10} is hydrogen or halogen, and

n is a number 0, 1 or 2,

with the proviso that R_9 , R_{10} , R_{11} , R_{12} and R_{13} are not all simultaneously hydrogen.

The compositions according to the invention preferably comprise as nickel complex pigment (A) a compound of formula (3)



wherein R_{14} and R_{15} are each independently of the other CN or halogen or together with the carbon atoms to which they are bonded form an aromatic ring that is unsubstituted or substituted by one or more nitro, cyano, hydroxy, $\text{C}_1-\text{C}_6\text{alkyl}$, amino or $\text{C}_1-\text{C}_6\text{alkylamino}$ groups or halogen atoms and

R_{16} to R_{23} are each independently of the others hydrogen, halogen, $-\text{NO}_2$, $-\text{CN}$, $-\text{OH}$, $-\text{COOH}$, $-\text{CH}_3$, $-\text{NH}_2$ or $-\text{NHCH}_3$.

An alkyl group as a substituent R_6 , R_7 , R_{11} , R_{12} , R_{13} , as part of a $-\text{CO}-\text{alkyl}$ group R_8 or as a substituent of any aromatic rings which may be present is, for example, methyl, ethyl,

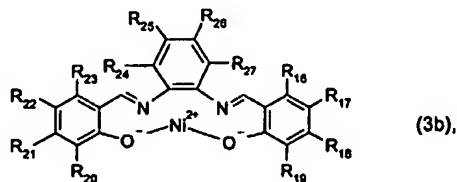
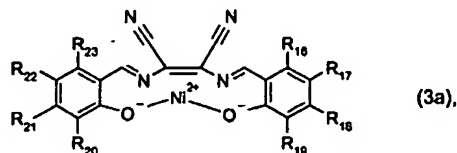
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propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, tert-amyl (1,1-dimethylpropyl), 1,1,3,3-tetramethylbutyl, hexyl, 2-methylpentyl, neopentyl, cyclopentyl, cyclohexyl, or a corresponding isomer.

Halogen is iodine, bromine or especially chlorine.

Among the optional substituents of rings A and B, special mention should be made of halogen, C₁-C₄alkyl and C₁-C₄alkoxy. One or more such substituents may be present.

Preferred nickel complex pigments of formula (3) are the compounds of formulae (3a) and (3b)

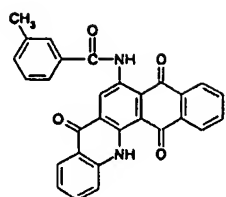


wherein R₁₆ to R₂₃ are as defined in claim 2 and R₂₄ to R₂₇ are each independently of the others hydrogen, halogen, -NO₂, -CN, -OH, -COOH, -CH₃, -NH₂ or -NHCH₃.

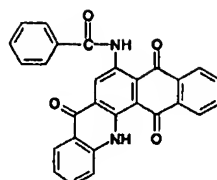
Special preference is given to compounds of formula (3a) wherein R₁₆ to R₂₃ are hydrogen and to compounds of formula (3b) wherein R₁₆ to R₂₇ are hydrogen.

Of the disperse dyes of formula (1), preference is given to the blue dyes of formulae (1a) - (1e)

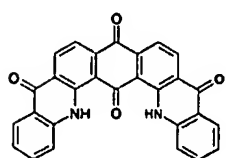
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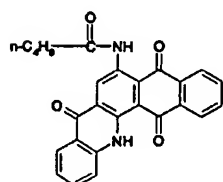
(1a).



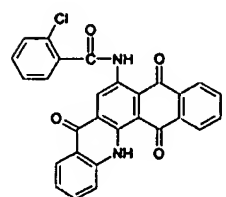
(1b).



(1c).

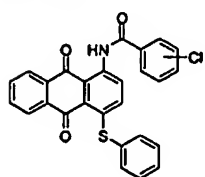


(1d).

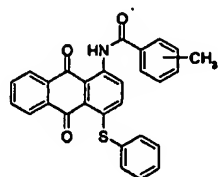


(1e).

Also preferred among the disperse dyes of formula (2) are the compounds of formulae (2a) - (2k)

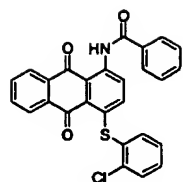


(2a).

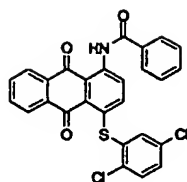


(2b).

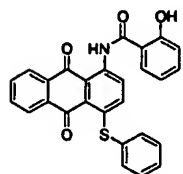
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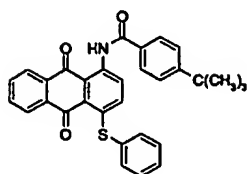
(2c),



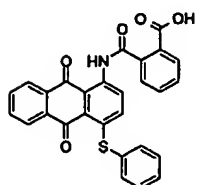
(2d),



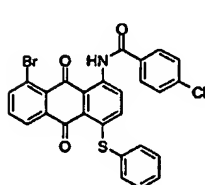
(2e),



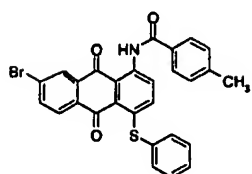
(2f),



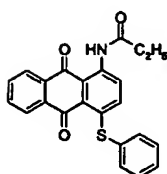
(2g),



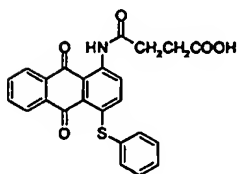
(2h),



(2i),



(2j),

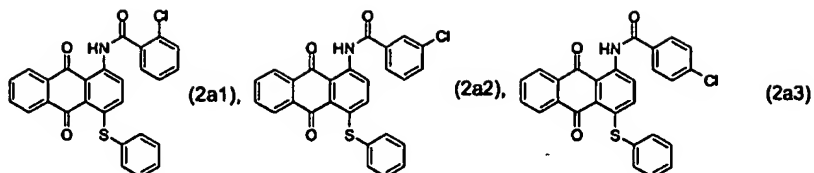


(2k).

Especially preferred disperse dyes (B) are the compounds of formulae (1a) and (2a).

The anthraquinone dye of formula (2a) is preferably used in the form of a mixture of the isomeric compounds (2a1), (2a2) and (2a3):

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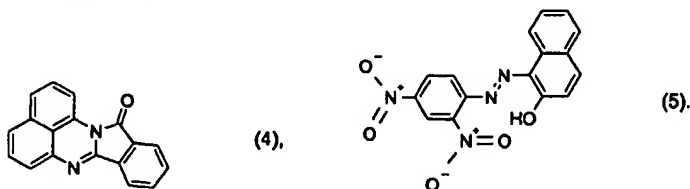


In that case the isomeric compounds (2a1), (2a2) and (2a3) are preferably present in approximately equal amounts.

The nickel complex pigments (A) used according to the invention are known and are described, for example, in WO 02/057537 and WO 02/055786.

The disperse dyes (B) are also known, for example from WO 02/051924 and WO 02/051942.

In a further embodiment, the compositions according to the invention comprise additionally (c) a pigment of formula (4) or (5)



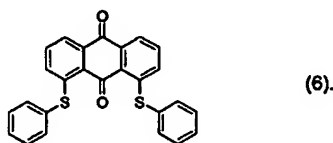
The disperse dyes of formulae (1) and (2) are suitable also for the production of mixed shades together with other dyes and especially together with a suitable yellow dye for trichromatic dyeing.

Trichromatic dyeing is to be understood as being the additive colour mixing of suitably selected yellow- or orange-dyeing, red-dyeing and blue-dyeing dyes with which any desired shade of the visible colour spectrum can be achieved by an appropriate choice of the relative proportions of the dye components.

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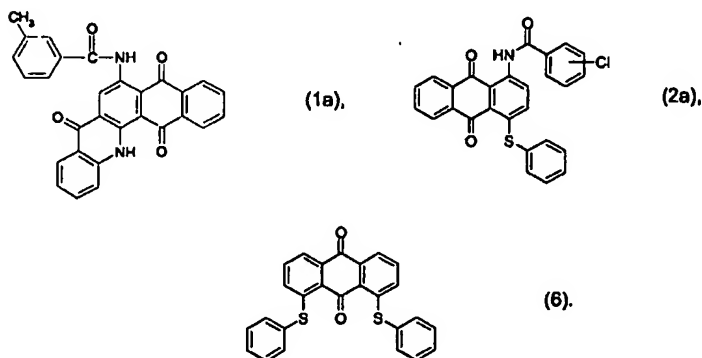
Since the compositions according to the invention can be used both in mass colouring and in the exhaust process or thermosol process, metamerism effects can be avoided.

The invention therefore relates also to compositions comprising as disperse dye (B) a trichromatic mixture comprising at least one blue-dyeing dye of the above formulae (1a) - (1e), at least one red-dyeing dye of the above formulae (2a) - (2k) and the yellow-dyeing dye of formula (6)



The dye of formula (6) has been known for a long time (C.I. Solvent Yellow 163) and is commercially available.

Special preference is given to trichromatic mixtures comprising the blue-dyeing dye of formula (1a), the red-dyeing dye of formula (2a) and the yellow-dyeing dye of formula (6)



The dye mixtures according to the invention can be used in the dyeing and printing of semi-synthetic and, especially, synthetic hydrophobic fibre materials, more especially textile materials. Textile materials composed of blends comprising such semi-synthetic and/or

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synthetic hydrophobic textile materials can likewise be dyed or printed using the dye mixtures according to the invention.

Semi-synthetic textile materials that come into consideration are especially cellulose 2¹/₂ acetate and cellulose triacetate.

Synthetic hydrophobic textile materials consist especially of linear, aromatic polyesters, for example those of terephthalic acid and glycols, especially ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane; of polycarbonates, e.g. those of α,α -dimethyl-4,4-dihydroxy-diphenylmethane and phosgene, and of fibres based on polyvinyl chloride and on polyamide.

The application of the dye mixtures according to the invention to the textile materials is effected in accordance with known dyeing procedures. For example, polyester fibre materials are dyed in the exhaust process from an aqueous dispersion in the presence of customary anionic or non-ionic dispersants and optionally customary swelling agents (carriers) at temperatures of from 80 to 140°C. Cellulose 2¹/₂ acetate is dyed preferably at about from 65 to 85°C and cellulose triacetate at temperatures of up to 115°C.

The dye mixtures according to the invention can also be used satisfactorily in the dyeing of polyester blends, for example polyester/cellulosic fibre blends.

The dye mixtures according to the invention are suitable for dyeing in accordance with the thermosol process, in the exhaust and continuous process and for printing processes. The exhaust process is preferred. The liquor ratio is dependent upon the nature of the apparatus, the substrate and the form of make-up. It may, however, be selected within a wide range, e.g. from 1:4 to 1:100, but is preferably from 1:6 to 1:25.

The said textile material can be in a variety of processing forms, e.g. in the form of fibres, yarns or non-wovens, in the form of woven fabrics or knitted fabrics.

It is advantageous to convert the dye mixtures according to the invention into a dye preparation prior to use. For this purpose, the dyes are ground so that their particle size is on average from 0.1 to 10 microns. The grinding can be carried out in the presence of dispersants. For example, the dried dye is ground with a dispersant or is kneaded into paste

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form with a dispersant and then dried *in vacuo* or by atomisation. The preparations so obtained can be used, after the addition of water, to prepare printing pastes and dyebaths.

For printing, the customary thickeners will be used, e.g. modified or unmodified natural products, for example alginates, British gum, gum arabic, crystal gum, locust bean flour, tragacanth, carboxymethylcellulose, hydroxyethylcellulose, starch or synthetic products, for example polyacrylamides, polyacrylic acid or copolymers thereof, or polyvinyl alcohols.

The dye mixtures according to the invention impart to the mentioned materials, especially to polyester material, level colour shades having very good in-use fastness properties, such as, especially, good fastness to light, more especially very good high-temperature light fastness, as well as a high level of fastness to wetting, such as fastness to water, perspiration and washing.

Especially high light-fastness properties can be achieved when the dye mixtures according to the invention additionally comprise UV absorbers.

The present invention relates also to the use of the compositions according to the invention in the production of coloured plastics or polymeric colour particles. The process for the production of coloured plastics or polymeric colour particles comprises mixing together a high molecular weight organic material and a tinctorially effective amount of a dye composition according to the invention.

The colouring of high molecular weight organic substances with the dye composition is carried out, for example, by mixing the dye composition into those substrates using roll mills, mixing apparatus or grinding apparatus, with the result that the dye composition is dissolved or finely dispersed in the high molecular weight material. The high molecular weight organic material with the admixed dye composition is then processed using methods known *per se*, for example calendering, compression moulding, extrusion, coating, spinning, casting or injection moulding, whereby the coloured material acquires its final form. It is also possible for the admixing of the dye composition to be carried out immediately prior to the actual processing step, e.g. by continuously feeding a dye composition in powder form and, at the same time, a granulated or pulverulent high molecular weight organic material, and optionally also additional ingredients, e.g. additives, directly into the intake zone of an extruder, where mixing takes place just before processing. In general, however, it is

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preferable for the dye composition to be mixed into the high molecular weight organic material beforehand, because more even colouration of the substrates can be obtained.

It is often desirable, in order to produce non-rigid mouldings or to reduce their brittleness, to incorporate so-called plasticisers into the high molecular weight compounds prior to shaping. There may be used as plasticisers, for example, esters of phosphoric acid, phthalic acid or sebacic acid. In the process according to the invention the plasticisers may be incorporated into the polymers before or after the incorporation of the colorant. It is also possible, in order to achieve different shades of colour, to add to the high molecular weight organic materials, in addition to the dye composition according to the invention, also further dyes or other colorants in any desired amounts, optionally together with further additives, e.g. fillers or siccatives.

Preference is given to the colouring of thermoplastic plastics, especially in the form of fibres. Preferred high molecular weight organic materials suitable for being coloured in accordance with the invention are very generally polymers having a dielectric constant of ≥ 2.5 , especially polyester, polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), polyamide, polyethylene, polypropylene, styrene/acrylonitrile (SAN) and acrylonitrile / butadiene / styrene (ABS). Polyester and polyamide are especially preferred. Very special preference is given to linear aromatic polyesters obtainable by polycondensation of terephthalic acid and glycols, especially ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane, for example polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT) or polybutylene terephthalate (PBTP); also polycarbonates, e.g. those of α,α -dimethyl-4,4-dihydroxy-diphenylmethane and phosgene, or polymers based on polyvinyl chloride and on polyamide, e.g. polyamide 6 or polyamide 6.6.

The following Examples serve to illustrate the invention. In the Examples, unless otherwise indicated, parts are parts by weight and percentages are percent by weight. The temperatures are given in degrees Celsius. The relationship between parts by weight and parts by volume is the same as that between grams and cubic centimetres.

Example 1:

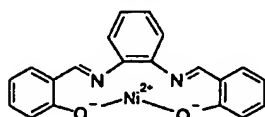
100 g of polyester fabric are immersed at room temperature in a liquor containing

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0.0037 g of the dye of formula (2a),

0.169 g of the dye of formula (1a),

0.561 g of the nickel complex pigment of formula (3b1),



(3b1),

1 g of ammonium sulfate and

0.5 g/l of a commercially available dispersant,

in 1000 ml of deionised water,

which has been adjusted to a pH of 4.0 – 5.0 with 80 % formic acid. The liquor is then initially heated to 135°C at a rate of 1°C/minute. After 30 minutes at 135°C, the liquor is cooled to 40°C, the dyed polyester fabric is washed with water and subjected to reduction clearing for 20 minutes at 70 - 80°C in a bath containing 5 ml/l of 30 % sodium hydroxide solution, 2 g/l of 85 % sodium dithionite solution and 1 g/l of a commercially available detergent. The finished dyeing is then washed with water and dried.

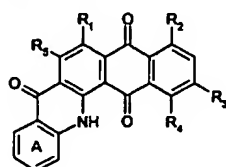
The resulting mid-grey dyeing has excellent light fastness and very good dry and wet fastness.

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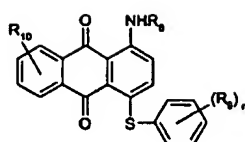
What is claimed is:

1. A composition comprising

- (A) at least one nickel complex pigment and
 (B) at least one disperse dye of formula (1) or (2)



(1),



(2),

wherein R_1 is hydrogen, hydroxy or a radical $-NHCO-R_6$ wherein R_6 is C_1-C_6 alkyl or unsubstituted or C_1-C_4 alkyl- or halo-substituted phenyl,

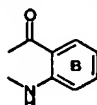
R_2 is hydrogen, hydroxy or a radical $W-R_7$ wherein W is $-NHCO-$ or $-S-$ and R_7 is C_1-C_6 alkyl or unsubstituted or C_1-C_4 alkyl- or halo-substituted phenyl,

R_3 is hydrogen,

R_4 is hydrogen or hydroxy,

R_5 is hydrogen, or

R_3 and R_4 together form the radical of formula



, wherein the rings A and B, independently of one another, may carry

further substituents,

R_6 is hydrogen or $-CO-C_2-C_6$ alkyl wherein the C_2-C_6 alkyl radical may be substituted

by carboxy, or a radical wherein R_{11} is hydrogen, C_1-C_4 alkyl,

hydroxy, carboxy or halogen, R_{12} is hydrogen, C_1-C_4 alkyl or halogen and R_{13} is hydrogen or C_2-C_3 alkyl or, when R_{10} is halogen, R_{13} may be methyl,

R_8 is hydrogen or halogen,

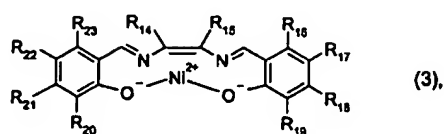
R_{10} is hydrogen or halogen, and

n is a number 0, 1 or 2,

with the proviso that R_6 , R_{10} , R_{11} , R_{12} and R_{13} are not all simultaneously hydrogen.

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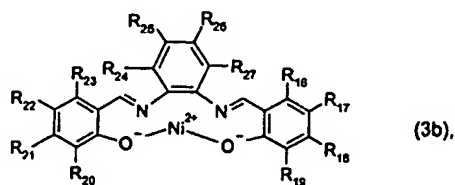
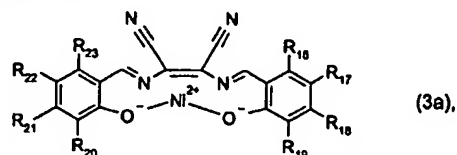
2. A composition according to claim 1, comprising as nickel complex pigment (A) a compound of formula (3)



wherein R_{14} and R_{15} are each independently of the other CN or halogen or together with the carbon atoms to which they are bonded form an aromatic ring that is unsubstituted or substituted by one or more nitro, cyano, hydroxy, C_1 - C_6 alkyl, amino or C_1 - C_6 alkylamino groups or halogen atoms and

R_{16} to R_{23} are each independently of the others hydrogen, halogen, $-NO_2$, $-CN$, $-OH$, $-COOH$, $-CH_3$, $-NH_2$ or $-NHCH_3$.

3. A composition according to claim 2, comprising as nickel complex pigment (A) a compound of formula (3a) or (3b)

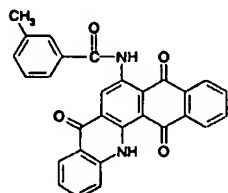


wherein R_{16} to R_{23} are as defined in claim 2 and R_{24} to R_{27} are each independently of the others hydrogen, halogen, $-NO_2$, $-CN$, $-OH$, $-COOH$, $-CH_3$, $-NH_2$ or $-NHCH_3$.

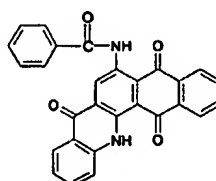
- 14 -

4. A composition according to claim 3, comprising as nickel complex pigment (A) a compound of formula (3a) wherein R_{18} to R_{23} are hydrogen or a compound of formula (3b) wherein R_{18} to R_{27} are hydrogen.

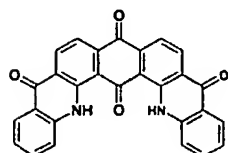
5. A composition according to claim 1, comprising as disperse dye (B) at least one compound of formulae (1a) – (1e)



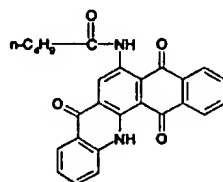
(1a),



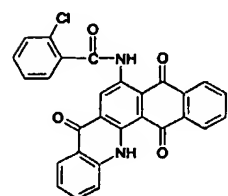
(1b),



(1c),



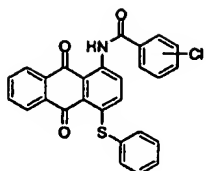
(1d),



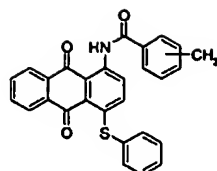
(1e).

6. A composition according to claim 1, comprising as disperse dye (B) at least one compound of formulae (2a) – (2k)

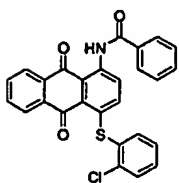
- 15 -



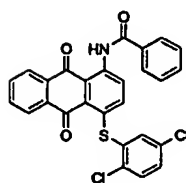
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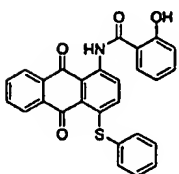
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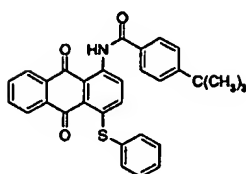
(2c),



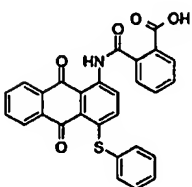
(2d),



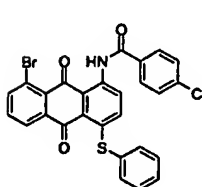
(2e),



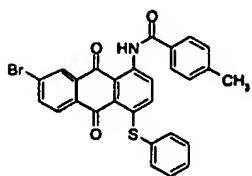
(2f),



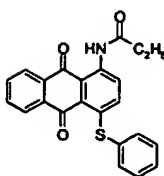
(2g),



(2h),

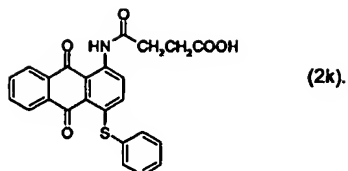


(2i),

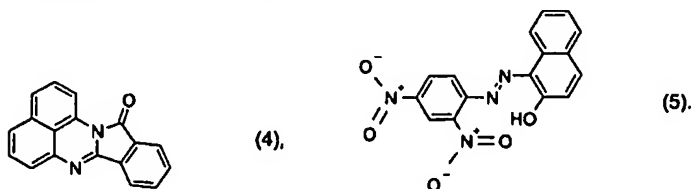


(2j),

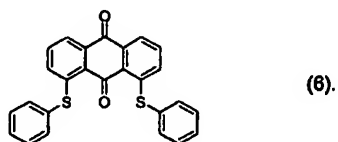
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7. A composition according to any one of the preceding claims, comprising additionally (c) a pigment of formula (4) or (5)



8. A composition according to claim 1, comprising as disperse dye (B) a trichromatic mixture comprising at least one blue-dyeing dye of formulae (1a) – (1e) according to claim 5, at least one red-dyeing dye of formulae (2a) – (2k) according to claim 6 and the yellow-dyeing dye of formula (6)



9. Use of a composition according to claim 1 in the dyeing or printing of semi-synthetic or synthetic hydrophobic fibre materials.

10. Use of a composition according to claim 1 in the production of coloured plastics or polymeric colour particles.

INTERNATIONAL SEARCH REPORT

International Application No
PC/EP2004/050515

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/051924 A (SUTTER PETER ;CIBA SC HOLDING AG (CH); HILDEBRAND RAINER (DE)) 4 July 2002 (2002-07-04) cited in the application page 8 - page 11; claims 1-3 -----	1-10
A	WO 02/055786 A (CLARIANT INT LTD ;SIEBER HELMUT (DE)) 18 July 2002 (2002-07-18) cited in the application claim 1 -----	1-10
A	WO 02/057537 A (CLARIANT INT LTD ;SIEBER HELMUT (DE)) 25 July 2002 (2002-07-25) cited in the application claim 1 -----	1-10
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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- *O* document referring to an oral disclosure, use, exhibition or other means
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- *S* document member of the same patent family

Date of the actual completion of the international search

22 July 2004

Date of mailing of the international search report

03/08/2004

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Authorized officer

Baston, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050515

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 265 632 A (PAPENFUHS THEODOR ET AL) 5 May 1981 (1981-05-05) claim 1	1-10
A	DE 274 357 C (FARBENFABRIKEN VORM. FRIEDR. BAYER & CO.) 18 May 1914 (1914-05-18) * Tabelle *	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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US 4265632 A	05-05-1981	NONE	
DE 274357 C		NONE	